Extraction of positive and negative ions from electron-beam-generated plasmas

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The results of investigations using pulsed, electron-beam-produced plasmas in Ar/SF_6 mixtures are reported. Time-resolved, positive, and negative ion fluxes were measured at a biased electrode located adjacent to the plasma. The measurements indicate that plasmas form with large negative ion densities due to electron attachment to SF_6 at the low electron temperatures associated with electron-beam-generated plasmas. [DOI: 10.1063/1.1498502]

In plasma-based microelectronic device fabrication, surface charging is found to produce damaging effects such as oxide breakdown and local side etching (notching) in high-aspect-ratio features.[1] It has been suggested[2–4] that ion–ion plasmas reduce surface charging by delivering anisotropic fluxes of both positive and negative ions to substrate surfaces. In ion–ion plasmas, negative ions replace electrons as the principle negative charge carrier, thereby reducing the confining sheath potential so that negative ions may leave the plasma. Kanakasabapathy *et al.*[2] have recently shown that alternating fluxes of positive and negative ions can indeed be extracted from ion–ion plasmas by applying a low-frequency bias to the substrate. Subsequently, they have shown[5] that etching with both positive and negative ions is possible.

Negative ions are formed in plasmas by electron attachment to neutral gas molecules and can exist in substantial quantities in electronegative gas plasmas.[6] The attachment rate varies with electron energy, and in halogen gases this rate increases with decreasing electron energy.[7] A requirement for the formation of ion–ion plasmas is that the attachment rate should be comparable to or greater than the gas ionization rate, in which case most electrons formed are soon converted to negative ions. This condition is typically met only during the afterglow of pulsed, halogen-based plasmas when the plasma density and electron temperature decrease to low values.[3,8] Of course, the plasma can not be sustained in the afterglow since the ionization rate is zero and as such, the time available for positive ion/negative ion flow from the plasma is limited.

Electron-beam-produced plasmas are found to have low electron temperatures and high plasma densities. For example, in molecular gases electron temperatures as low as 0.3 eV and plasma densities in excess of 10^{11} cm^{-3} over the volume of the beam have been measured.[9] Hence, electron-beam-generated plasmas offer a novel approach for producing continuous ion–ion plasmas and thus a means to provide constant fluxes of positive and negative ions. In this ''proof-of-principle'' investigation, we report the experimental results using modulated electron-beam-generated plasmas in 50:50 mixtures of Ar and SF_6. The goals were to (1) produce plasmas with large negative ion concentrations during the active phase of the pulsed plasma and (2) extract both positive and negative ions. We present time-resolved ion fluxes at a biased electrode located adjacent to the beam.

The experiments were performed in the Naval Research Laboratory's large-area plasma processing system which utilizes a magnetically collimated, high-energy electron beam to ionize the background gas. The experimental apparatus, schematically represented in Fig. 1, is similar to the apparatus previously described,[10] except these experiments were performed in a rectangular, stainless-steel chamber with a base pressure of 10^{-8} Torr and the 150 G field was generated using a solenoidal coil.

The electron beam is extracted from a linear hollow cathode. The emergent beam, collimated by the magnetic field, enters the experimental region through a slot in a grounded anode. For all measurements reported here, the beam pulse was 1 ms long with a repetition rate of 50 Hz, and the beam energy was nominally 2 kV. The partial pres-

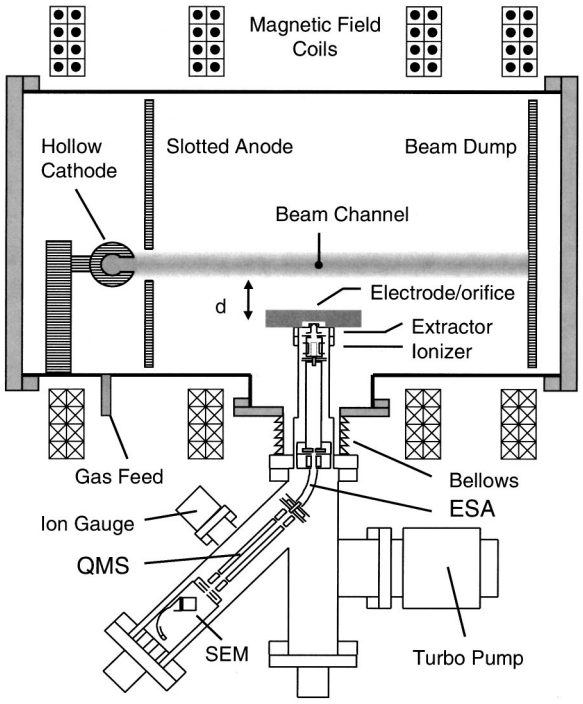

FIG. 1. Schematic diagram of the chamber and the plasma probe. The probe consists of an ESA in series with a QMS.

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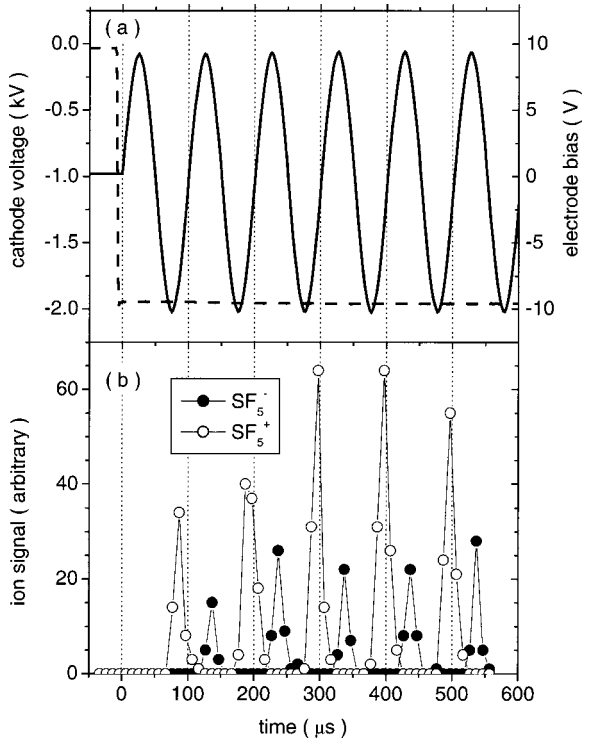

FIG. 2. (a) The applied voltage to the cathode (dashed) and the low-frequency electrode bias (solid). (b) The flux of SF_5^- and SF_5^+.

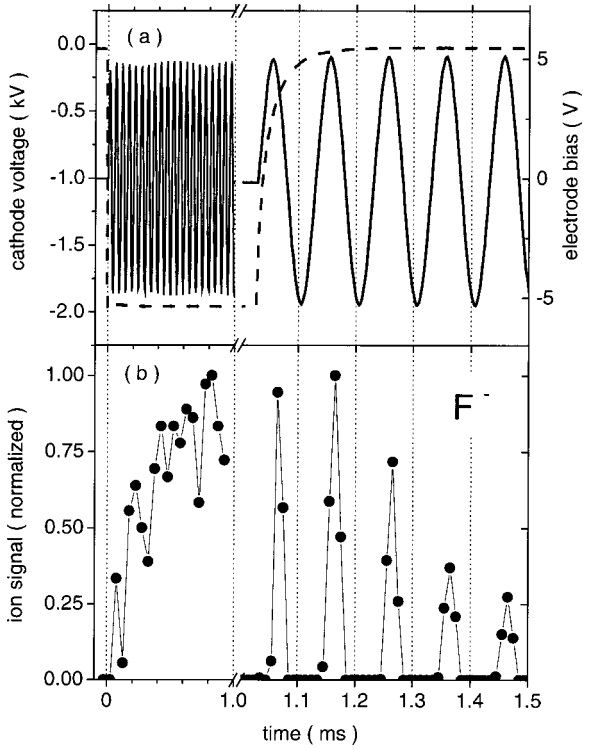

FIG. 3. (a) The applied voltage to the cathode (dashed) and the electrode bias (solid). The applied bias frequency during the pulse (0–1 ms) is 20 kHz and after the pulse it is 10 kHz. (b) The extracted F^- flux.

sures of Ar and SF_6 were each 35 mTorr (70 mTorr total pressure).

Ion fluxes and energy distributions were measured at a 5.7 cm diameter stainless-steel electrode located 1 cm from the beam edge. The measurements were performed using a Hiden EQP 300 Plasma Probe (Fig. 1). The probe is differentially pumped and consists of an electrostatic ion-energy analyzer (ESA) in series with a quadrupole mass spectrometer (QMS). Ions enter the EQP through a 50 μm diameter aperture located in the center of the electrode and are then energy selected and mass filtered prior to detection by a channeltron secondary-electron multiplier (SEM). The probe has not been calibrated to determine the absolute flux so the intensity of the measured signal is reported in arbitrary units.

Time resolution was achieved using a scanning gate on the EQP output (SEM). The ESA was set to select energies that maximized the ion signal intensity over a given time period. For all measurements, the passband of the ESA was fixed at ± 0.5 eV. A gate of the SEM signal was then scanned in equal increments to obtain the temporal flux measurements, with the signal accumulated over several hundred pulses to achieve a reasonable signal-to-noise ratio. Details of time-resolved measurements using the EQP probe have been described elsewhere.[11]

Shown in Fig. 2 are the temporal profiles of positive and negative ions incident to the electrode during part of the electron-beam pulse along with the applied electrode bias. The cathode pulse, which defines the active phase, extends from 0 to 1 ms and is shown by a dashed line in Fig. 2(a). Also shown in Fig. 2(a) is the sinusoidal bias applied to the electrode (10 kHz, ± 10 V). The SF_5^+ and SF_5^- signals shown in Fig. 2(b) were collected during a 10 μs wide gate that was scanned in steps of 10 μs. It should be noted that the time of flight through the EQP is a function of the ion mass and charge. We have estimated the time of flight to be ≈ 50 μs for F and ≈ 150 μs for SF_5 ions, and the time scale was adjusted accordingly. Species of equal mass were chosen in Fig. 2 to avoid errors associated with these estimates.

From the data in Fig. 2, it is clear that positive ions (SF_5^+) are collected when the electrode bias is negative and negative ions (SF_5^-) are collected when the bias is positive. SF_5^- is not observed during the first positive swing in the applied bias, presumably because the plasma must first achieve conditions favorable for the production and/or extraction of negative ions.[12] The difference in intensities between the ion species is due to the fact that SF_5^+ is the dominant positive ion while SF_5^- is not the dominant negative ion. The measured cations in order of significance are SF_5^+, SF_3^+, and Ar^+ while the anions are SF_6^-, SF_5^-, and F^-, respectively. The relative intensities of the various ion species are in line with creation of cations by high-energy electron impact ionization[13] and anions via low-energy electron attachment[14] in SF_6.

The extraction of negative ions is not limited to a particular phase of the pulsed plasma. The F^- signal along with the applied bias is shown in Fig. 3 for both the active plasma ($t \leqslant 1$ ms) and afterglow ($t > 1$ ms) phases. During the active phase, a 20 kHz (± 5 V) bias was applied to the electrode and the anions were collected during a 50 μs window that was synchronized with the positive phase of the applied bias. During the afterglow, a 10 kHz (± 5 V) extraction bias was used and the signal was accumulated as before. The F^- signals are normalized to the peak intensity in each phase so as to compare signals. It is important to note that since the anion signal is energy resolved (± 0.5 eV), the signal is not necessarily indicative of total flux. Nonetheless, the F^- sig-

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nal is clearly present during the active phase and then decays during the afterglow. Here again, the onset of the anion signal does not occur until ~100 μs after the beginning of the cathode pulse.

The ability to extract both positive and negative ions is a good indication that ion–ion plasmas have been formed in the active phase. The transition toward ion–ion plasmas was verified in separate experiments,[15] where the SF_6 concentration was varied between 0% and ~13%. Specifically, Langmuir probe characteristics show an increasing symmetry about the current axis, suggesting an increasing negative ion density.[8] Furthermore, microwave transmission measurements indicated the electron density for mixtures containing only 13% SF_6 was at least two orders of magnitude lower than the electron density in pure argon.

In summary, electron-beam-generated plasmas have been produced in Ar/SF_6 mixtures that contain significant amounts of negative ions. Using an alternating, low-frequency bias, both positive and negative ions were extracted during the active phase of plasma production. Clearly, more experiments are needed to understand the dynamics of beam produced plasmas containing SF_6 and to verify the production of ion–ion plasmas. However, these preliminary results show that it is possible to generate plasmas in electronegative gases with low attachment thresholds that exhibit significant negative ion densities and to extract both positive and negative ions during all phases of plasma production.

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